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PHYSICAL-CHEMICAL AND STRUCTURAL PROCESSES OCCURRING DURING HEAT-TREATMENT OF STRONTIUM-ALUMINOSILICATE GLASS

N. E. Shchegoleva,¹ P. D. Sarkisov,² L. A. Orlova,² and N. V. Popovich²

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The results of synchronous thermal, x-ray phase, electronic paramagnetic resonance, and optical spectroscopy analyses of the physical-chemical and structural processes occurring during the heat treatment of strontium-aluminosilicate glass are presented. The dependence of structure-formation processes on the chemical composition of the glass is studied.

Key words: glass, pyroceramic, crystallization, liquation, anortite.

The prospects for obtaining anortite, cordierite, celsian and spodumene pyroceramics are due to the uniqueness of the physical-mechanical and dielectric properties that materials acquire in the process of directed crystallization, which opens up the possibility of using them as radioparent materials in aviation technology. The system $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ is of scientific and practical interest from the standpoint of synthesizing pyroceramics possessing simultaneously improved dielectric properties, high mechanical strength, chemical stability and heat-resistance owing to the properties of the crystalline phase — strontium anortite, which is released when glass is ceramitized. The melting temperature of strontium aluminosilicate (1760°C) is much higher than that of spodumene, eucryptite and cordierite, which are used to synthesize technical pyroceramics for industrial applications [1, 2].

The present article reports the results of studies of the physical-chemical and structural processes occurring during the heat-treatment of glass with strontium-aluminosilicate composition for obtaining high-temperature radioparent pyroceramics.

Glasses in the system $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ with titanium dioxide as the crystallization catalyst were chosen to investigate the possibility of obtaining pyroceramics with the required dielectric characteristics and high working temperature (to 1200°C). This choice of glass compositions is due to the fact that monoclinic strontium anortite has been identified as the dominant crystalline phase in them. The compo-

nent ratios of the experimental glasses was determined on the basis of the work performed by N. M. Bobkova, L. M. Silich, and B. G. Varshal in a manner so that the chosen glasses would meet a complex of technological requirements — first and foremost the melting temperature of the initial glass, which must not exceed 1600°C, and a low upper temperature limit of crystallization (no higher than 1450°C). The phase composition of the crystallized material must be comprised principally of monoclinic strontium anortite. On the other hand, there is only a limited possibility of introducing into the composition of the glass TiO_2 as a crystallization catalyst because an increase of the mass fraction of this oxide will increase the dielectric constant, which is most strongly manifested in pyroceramics and decreases the radioparency of the material. The compositions of the synthesized glasses are presented in Table 1.

Of the compositions chosen, SAS-2 and SAS-4 are distinguished by the fact that the molar ratio $\text{Al}_2\text{O}_3 : \text{SrO} = 1 : 1$; hence, in crystallization process both oxides will completely transform into the crystalline phase (strontium

TABLE 1. Compositions of the Glasses Studied

Glass	Oxide content, wt. %			
	SiO_2	Al_2O_3	SrO	TiO_2
SAS-1*	36.3	30.8	19.5	13.4
SAS-2	45.5	20.0	19.5	15.0
SAS-4	40.0	22.5	22.5	15.0
SAS-6	40.0	30.0	20.0	10.0

* Glass crystallized during pouring.

¹ Federal State Unitary Enterprise — All-Russia Scientific-Research Institute of Aviation Materials (FGUP VIAM), Moscow, Russia (e-mail: admin@viam.ru).

² D. I. Mendeleev Russian Chemical Technology University (RKhTU im. D. I. Mendeleeva), Moscow, Russia.

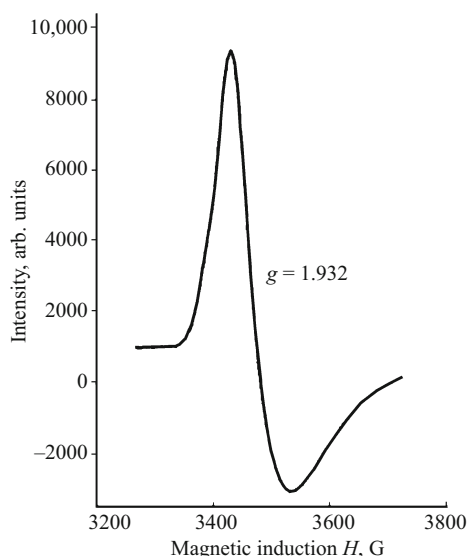


Fig. 1. EPR spectrum of SAS-6 glass heat-treated at 850°C.

anortite $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), while the residual glass phase will be represented by SiO_2 , which should make the material resistive to aggressive media. On the other hand, these glass compositions require introducing fluxing agents, such as titanium dioxide. The SAS-1 composition is also distinguished by a high content of a crystallization catalyst. Because high TiO_2 concentrations are critical to attain the required level of the dielectric characteristics of pyroceramics the composition of SAS-6 glass, in which the content of the crystallization catalyst is reduced, was also examined. In this case the molar ratio $\text{Al}_2\text{O}_3 : \text{SrO} > 1$. However, this is less significant, since in the crystallization process all SrO and a large fraction of Al_2O_3 will convert to anortite, while the residual glass phase will consist of high-silica aluminosilicate glass, which likewise has good chemical stability. In addition, in this case aluminotitanate phases are more likely to be formed than rutile, which is more favorable for reaching the required dielectric properties.

The glassmaking was conducted in a gas-flame furnace under the following conditions: oxidative glassmaking conditions; glassmaking temperature 1600°C; glassmaking time at maximum temperature about 4 h; annealing temperature 650°C.

It was established that the SAS-2 and SAS-4 compositions have the best glassmaking capacity.

The color of the glasses ranges from yellow (SAS-6) to brown (SAS-2 and SAS-4). The studies have shown that the color is due to the formation of complexes with the participation of iron present in the form of impurities in the initial components of the mix, since glass made from pure components in an oxidative environment is colorless even at high TiO_2 concentrations. During glassmaking under oxidative conditions the Ti^{3+} ions formed as a result of possible thermal dissociation are oxidized once again to the tetravalent

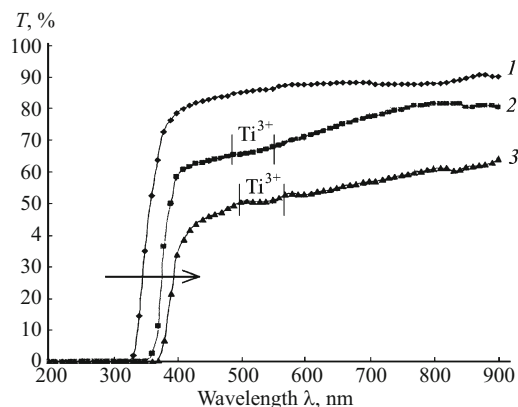


Fig. 2. Optical absorption spectra of SAS-6 glass: 1) glass without heat-treatment; 2, 3) glass heat-treated at 850 and 960°C, respectively.

state [3]. The EPR spectra of the glass samples showed the presence in the SAS-2 and -4 glasses of trivalent titanium in an axially distorted octahedral environment, as the presence of signal with g -factor 1.94 shows. Titanium Ti^{3+} is capable of forming with iron ions complexes of the type $\text{Ti}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}$, which give rise to sharp darkening of the glass [4–8].

The crystallizability of the glass was studied in a wide temperature interval by mass crystallization using successive heat-treatments and visual examination of the glass samples using simultaneously differential scanning calorimetry (DSC) and x-ray phase analysis (XPA). As temperature increases, deep structural changes occur in all synthesized glasses, visually accompanied by darkening and then by opalescence, which transforms into crystallization with white material being obtained.

Color intensification occurring during heat treatment is due to the character of the nonuniform microstructure. Metastable liquation, giving rise to segregation of the iron and titanium cations in one of the phases, can in this way lead to an effective increase of their concentration in this liquid phase, a decrease of the distance between the cations and an increase of the probability of formation of additional color complexes. This suggests that, as will be shown below, the structural rearrangements for SAS-2 and -4 glasses occurred at the cooling stage, and the darker color attests to liquation.

The reduced titanium ions Ti^{3+} , giving rise to darkening, for the SAS-6 glass are detected by EPR (Fig. 1) but only during heat-treatment, when structural rearrangements are starting (the signal with g -factor 1.932 in the EPR spectrum). The Ti^{3+} ions are also recorded by optical spectroscopy (Fig. 2) in the form of absorption bands in the optical absorption spectrum T in the wavelength range 500–550 nm. The shift of the absorption band into the long-wavelength region in the spectra attests to the presence of Fe^{3+} and the formation of complexes of several transition elements.

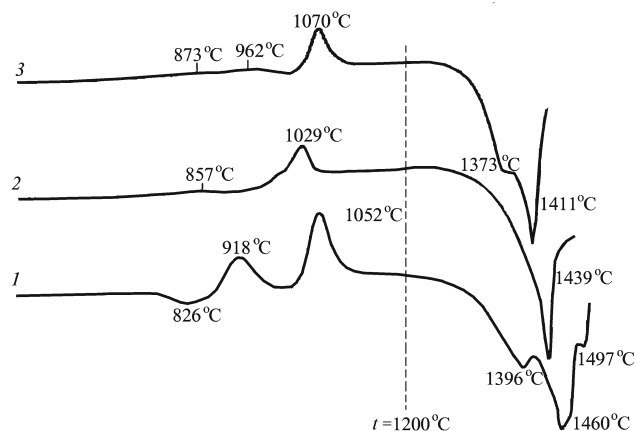


Fig. 3. DSC results for strontium aluminosilicate glass: 1, 2, 3) SAS-6, -4, and -2, respectively.

The blue and brown hues of the crystallized samples indicate that the color centers present in the initial glass and giving rise to further darkening with increasing heat-treatment temperature remain in the course of the entire crystallization process [4, 6, 7].

X-ray phase analysis and DSC showed that a decrease of the TiO_2 weight content in the glass and deviation from the molar ratio of aluminum oxide to the alkaline-earth metal (MO) $\text{Al}_2\text{O}_3 : \text{MO} = 1 : 1$ increase the crystallization onset temperature and change the enthalpy of the process and character of phase formation. Figure 3 shows the results of the DSC analysis of the glasses.

Endothermal and exothermal peaks are clearly seen in the DSC curves. An endoeffect at low temperatures (826°C) is observed for the SAS-6 composition. The appearance of an endothermal effect during the precrystallization period can be interpreted differently. Many authors attribute its appearance to a change of the rate of structural rearrangements or structural transformations occurring in the vitrification interval. This can be a rupture of weak ionic bonds of modifier cations with non-bridge oxygen in the framework or between components of the structural framework or a change of the ion interaction energies [9].

Studying $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ glass the authors of [10] attribute the appearance of an endoeffect in the vitrification region to the absorption of structural heat required to activate the crystallization process.

For the SAS-6 composition, the presence of the indicated effect is also attributed to the absorption of the energy required to activate crystallization.

The absence of endothermal effects during the precrystallization period in the DSC curves for SAS-2 and -4 glass is explained by their chemical composition, specifically, the high TiO_2 content. As a result of the active interaction of titanium oxide with aluminum oxide liquation and structural rearrangements occur in them even during cooling, while amorphized structures fully ready for crystallization can be present in the initial glasses. The proof of this is the darker

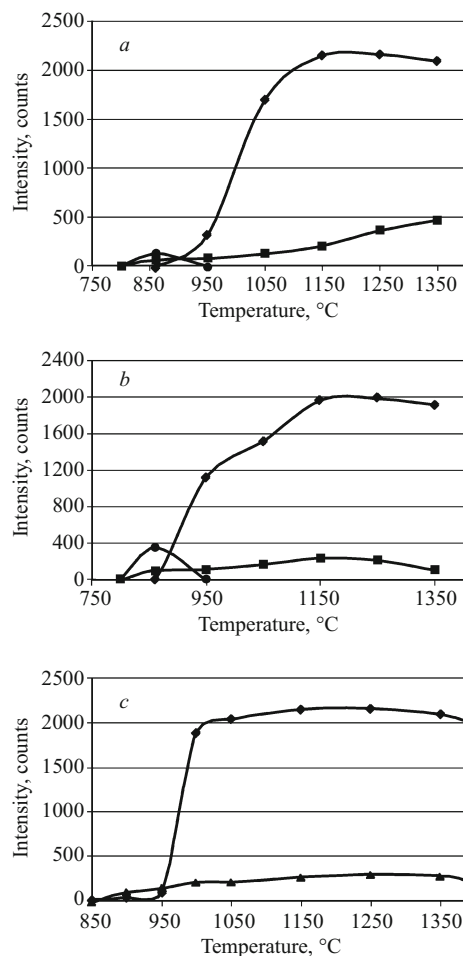


Fig. 4. Crystallization intensity versus the one-step heat-treatment temperatures of the glasses: a, b, c) SAS-2, SAS-4 and SAS-6, respectively; 1) monoclinic strontium anortite; 2) rutile; 3) hexagonal strontium anortite; 4) tialite.

color of the glass due to the high concentration of the color centers, small magnitude of the exo peaks and heat effects corresponding to the formation of titanium-containing phases, as well as the character of the x-ray diffraction patterns consisting of an amorphous halo with diffuse diffraction peaks. Since the structure of these glasses is completely ready for a transition into the crystalline state, they do not require additional heat input for activation of crystallization, so that there is no endo effect. For them, crystallization starts at 820 and 810°C (the first exothermal peaks at 873 and 857°C), respectively, and is characterized by low enthalpies. The temperature difference between the onset of the crystallization process for these compositions can be explained by the effect of SiO_2 , an increase in whose content results in a more viscous glass and, in consequence, retardation of structural rearrangements. According to the data of [4], an increase of the content of titanium oxide in the glass results in a shift of the crystallization onset temperature toward lower temperatures. The same behavior is observed in the present work.

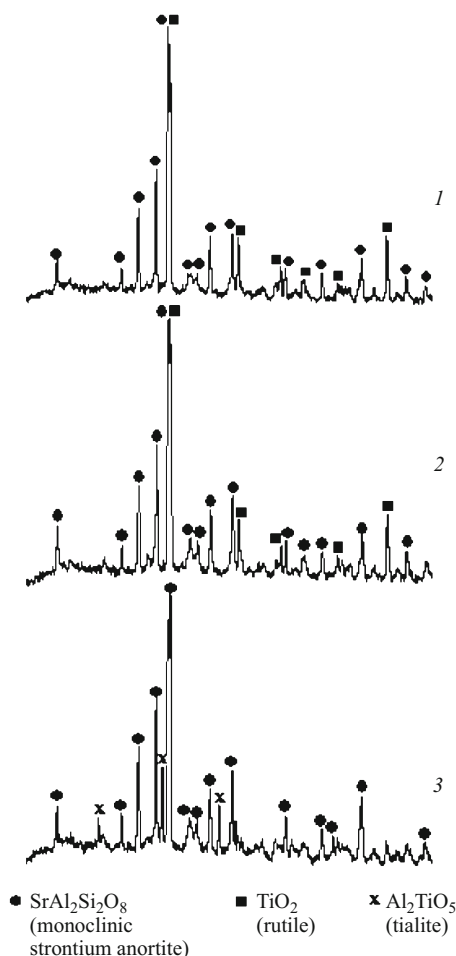


Fig. 5. X-ray diffraction patterns of glasses heat-treated at 1350°C: 1, 2, 3) SAS-2, SAS-4, SAS-6, respectively.

For the SAS-6 composition, where the TiO_2 content is lowered to 10 wt.%, while the molar ratio $\text{Al}_2\text{O}_3 : \text{MO} = 3 : 2$, crystallization starts at 870°C (peak at 918°C). The endothermal effects in the temperature interval 1350–1500°C correspond to softening of the residual glass phase and dissolution of the crystalline phases.

The curves of the intensity of the crystallization of the phases versus the temperature of the single-step heat-treatment of the glasses are displayed in Fig. 4. A combined analysis of the XPA (Fig. 5) and DSC results revealed the effect of the chemical composition on the temperature intervals and sequence of the formation of crystalline phases in the heat-treatment processes. It was established that the nature of the initially released crystalline phase — rutile or tialite — depends on the molar ratio $\text{Al}_2\text{O}_3 : \text{SrO}$ and the TiO_2 concentration; this determines the form of the strontium anortite precipitated — hexagonal or monoclinic.

Thus, since the molar oxide ratio $\text{Al}_2\text{O}_3 : \text{SrO}$ in SAS-2 and -4 glasses is 1 : 1 and the TiO_2 content is high, rutile and the simplest hexagonal form of strontium anortite precipitate at the first stages of heat-treatment. Even though the liqua-

tion process is accompanied by an active interaction of titanium and aluminum oxides, aluminotitanate crystalline phases are not formed because all of the aluminum oxide goes to the formation of the structural network of anortite, for which the molar ratio is $\text{SrO} : \text{Al}_2\text{O}_3 : \text{SiO}_2 = 1 : 1 : 2$.

For the SAS-6 composition, where the molar ratio of the oxides $\text{Al}_2\text{O}_3 : \text{SrO}$ exceeds 1, tialite as the primary crystalline phase and then monoclinic anortite form. Tialite crystallizes out of the aluminotitanium glass phase, which is highly prone to crystallization, at the early stages of heat-treatment.

As the temperature increases, a polymorphic transformation of hexagonal anortite into the monoclinic modification (exothermal peaks at 1070 and 1029°C, respectively, in Fig. 3) is observed in the glasses SAS-2 and -4, since the first one is unstable because it requires the presence of strontium ions with the coordination number 12, and crystallization of monoclinic anortite from the glass phase is also observed. For SAS-6 glass, the exo peak at 1052°C in Fig. 3 corresponds to the crystallization of the monoclinic form of anortite (by-passing the formation of the hexagonal phase). As the heat-treatment temperature is further increased, the phase composition of the materials remains unchanged (see Fig. 4).

It is known that the temperature range where tialite exists in its pure form consists of two sections: 20–750°C and 1300–1820°C. At 750–1300°C it decomposes into corundum and rutile. Such instability of this phase can be controlled by introducing stabilizing additives, such as, specifically, alkaline-earth metal oxides, silicon oxide, and others. The presence of oxides such as SrO and SiO_2 in the glass also affected the stability of tialite in the entire temperature interval of heat-treatment of SAS-6 glass.

According to these studies, the composition of SAS-6 glass can be regarded as the main one in the strontium aluminosilicate system for obtaining high-temperature radioparent pyroceramics. The absence of rutile in the material eliminates the possibility of increasing the dielectric constant above the required values, while the absence of hexagonal anortite precludes any increase of the CLTE and possible phase transition into the orthorhombic form, which is accompanied by a change of the volume to 3% and therefore the possible formation of microcracks and strength losses. For SAS-6, higher softening temperatures of the residual glass phase and dissolution of the crystalline phases in it are also characteristic; this shows the substantial advantage of and possibility of attaining high working temperatures for pyroceramics based on it.

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